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Department of Chemical and Metallurgical
Engineering

University of Tennessee

Knoxville, Tennessee

SEMI-ANNUAL PROGRESS REPORT
ON THE APPLICATION OF DIFFUSE
X-RAY SCATTERING TO THE STUDY
OF THE STRUCTURE OF BINARY
ALLOYS

March 1, 1966 - August 31, 1966

NASA Grant NGR-43-001-018

Submitted to

National Aeronautics and Space Administration

Washington, D. C., 20546

Submitted by

J. E. Spruiell

GPO PRICE \$ _____

CFSTI PRICE(S) \$ _____

Hard copy (HC) 1.50

Microfiche (MF) .50

653 July 85

N66 39910

FACILITY FORM 102

13
(PAGES)
CB 79124
(NASA CR OR TMX OR AD NUMBER)

1
(THRU)
17
(CODE)
17
(CATEGORY)

I. INTRODUCTION

The research in progress under this grant (NASA Grant NGR-43-001-018) consists of an experimental and theoretical investigation of the relationship between the local atomic arrangements in metallic solid solutions and the physical, mechanical, and thermodynamic properties of the solid solutions. Alloys from three systems have been chosen for study during the initial stages of this research. These systems are the Ni-Pd system, the Fe-Al system, and the Ni-W system. The present status report outlines the research carried out with respect to each of these systems during the period March 1, 1966 to August 31, 1966.

II. THE NICKEL-PALLADIUM SYSTEM

A Ni-Pd single crystal of composition 50 at. % Ni was grown by the Bridgman technique using the equipment described in a previous status report (1). In this equipment a vacuum of approximately 10^{-5} torr is maintained in the chamber containing the sample. The growth rate of the crystal was about 1-inch per hour. After the crystal was grown, it was held for 96 hours at 1100°C in order to homogenize it. Both metallographic examination and x-ray diffraction evidence (Debye-Scherrer patterns of filings and Laue patterns) indicated that no macroscopic segregation or coring remained in the crystal after the homogenization treatment.

The orientation of the crystallographic axes was located by the back-reflection Laue technique and a 1/8-inch thick disc was cut from the crystal with an approximately (210) face. This disc was metallographically prepared and aligned on the x-ray diffractometer within a cryostat and vacuum chamber.

X-ray diffuse scattering measurements were made in the h_1h_20 plane of reciprocal space at 300°K and at 86°K. The measurements made at 300°K are presented in Figure 1. The intensity units are arbitrary and the measurements shown have not been corrected for Compton modified scattering or temperature diffuse scattering. Contours greater than 70 near the 200 and 220 Bragg peaks have been omitted.

The most obvious features of Figure 1 are the diffuse maxima near the 1.5 00, 2 1.5 0, and 110 positions. It is indeed interesting that the maxima near 110 is approximately one-half as intense as the maxima near 1.5 00. There is no evidence for any peaking of the diffuse intensity at positions such as 100, 210, or 300, although the intensity is not negligible at these positions due to the overlap of the maxima centered near 1.5 00, 2 1.5 0, and 3.5 00. These facts would seem to imply that the cause of the scattering is not short range order, since even a slightly negative value of the first neighbor local order parameter, α_{110} , would produce a weak diffuse maximum of equal intensity at all positions of mixed (odd and even) indices. However, at the present time it is not possible to be certain of this interpretation.

Assuming that the diffuse scattering distribution shown in Figure 1 is not due to short range order, what, then, could be its origin? In general we may say that a large atomic size effect, or clustering, or both could cause the modulations of the intensity observed in the data of Figure 1. Furthermore, only the atomic size effect can produce an asymmetric distribution about a Bragg peak such as is observed about the 200. Thus there is definitely a large atomic size effect indicated by the data. It is not likely, however, that the distribution is caused by the size effect alone due to the existence of the peaks at 110 and 310. The observed intensity distribution

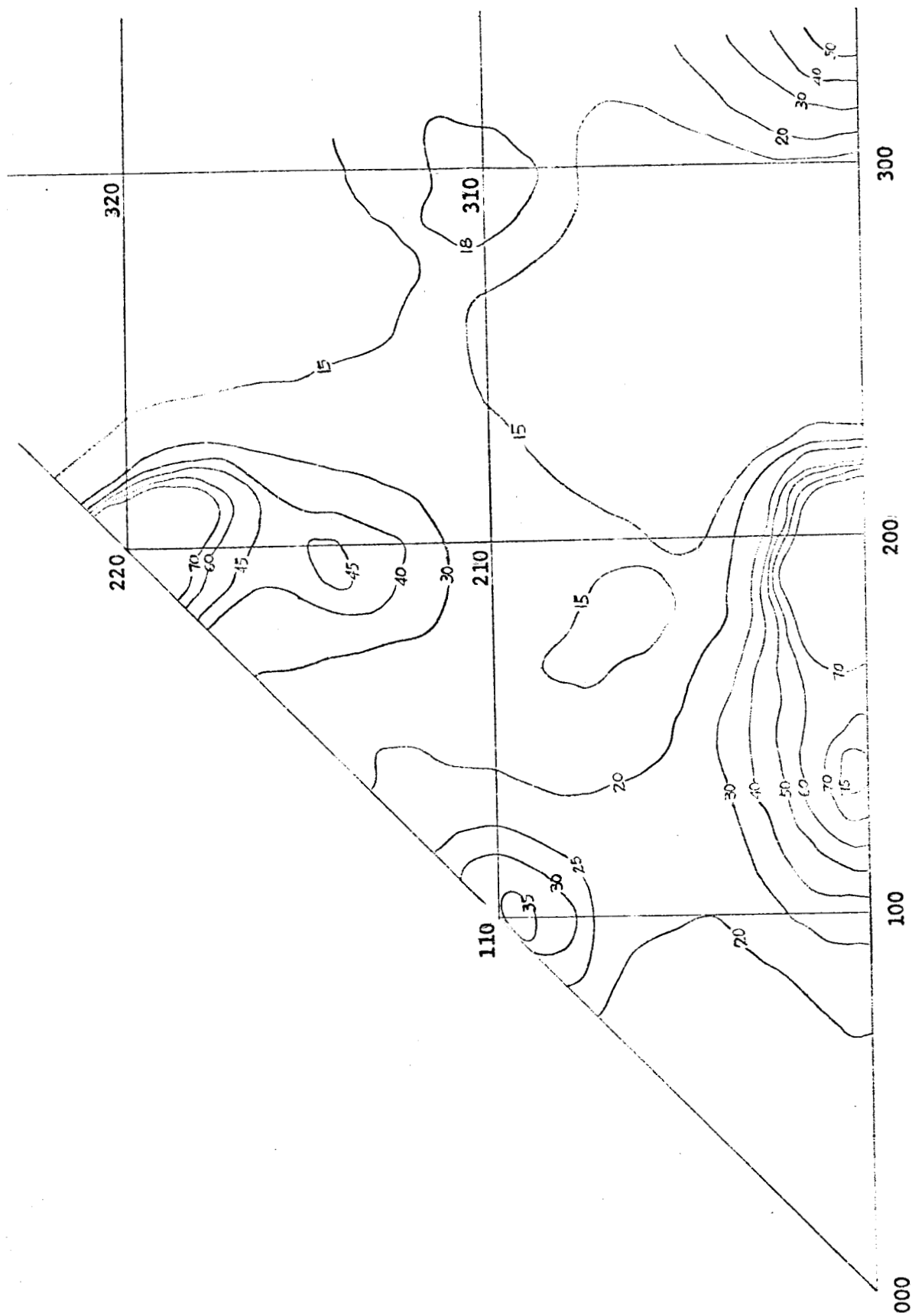


Figure 1. Diffuse intensity distribution on the h_1h_20 plane of reciprocal space for a Ni -50 at. % Pd crystal.

is, therefore, likely due to a combination of clustering and the atomic size effect. In any case, the remarks made here must be considered to be preliminary. A more detailed analysis of the data must be carried out before the very unusual intensity distribution presented in Figure 1 can be completely understood.

III. THE IRON-ALUMINUM SYSTEM

In our last status report (1) some preliminary diffuse scattering data from an Fe -14.5 at. % Al single crystal were discussed. During the present report period we have completed numerous measurements of the diffuse scattering from the Fe -14.5 at. % Al crystal and also from an Fe -19.2 at. % Al crystal. A list of the sample conditions and type of data collected is presented in Table I. For some heat treatments measurements have been made throughout a plane in reciprocal space at two temperatures: room temperature (300°K) and approximately 136°K. For other heat treatments data have been collected only along the h_100 line in reciprocal space at 300°K. This approach was used so that the effects of numerous heat treatments could be evaluated in a reasonable time.

Figure 2 shows the variation in the diffuse scattering along the h_100 line in reciprocal space in the neighborhood of the 100 position for different heat treatments of the Fe - 19.2 at. % Al crystal. The letters labeling the various curves refer to the heat treatments presented in Table I. These data indicate that annealing at 250°C following a quench from a high temperature causes the state of the sample to gradually change from one in which only short range order exists to one in which essentially

TABLE I
DIFFUSE SCATTERING MEASUREMENTS COMPLETED FOR THE IRON-ALUMINUM SYSTEM

| Crystal | Heat treatment of sample* | Range of Data Collected |
|-------------------|---|--|
| Fe -14.5 at. % Al | a) Annealed 50 hours at 1000°C, furnace cooled to 100°C, quenched to r.t. | h ₁ h ₂ 0 plane at r.t. |
| | b) Annealed 8 hours at 850°C, furnace cooled to 300°C, annealed 80 hours at 300°C, quenched to r.t. | h ₁ h ₂ 0 plane at r.t. |
| | c) Annealed 5 hours at 850°C, quenched to r.t., annealed 1 week at 250°C, quenched to r.t. | h ₁ h ₂ 0 plane at r.t. and 136°K |
| Fe -19.2 at. % Al | a) Annealed 8 hours at 850°C, quenched | h ₁ h ₂ 0 plane r.t. data only |
| | b) Annealed 8 hours at 850°C, quenched, annealed 1 hour at 250°C, quenched | h ₁ 00 line r.t. data only |
| | c) Annealed 8 hours at 850°C, quenched, annealed 1 hour at 250°C, quenched, annealed 5 hours at 250°C, quenched | h ₁ 00 line r.t. data only |
| | d) Annealed 8 hours at 850°C, quenched, annealed 1 hour at 250°C, quenched, annealed 9 hours at 250°C, quenched | h ₁ 00 line r.t. data only |
| | e) d) + annealed 20 hours at 250°C, quenched | h ₁ 00 line r.t. data only |
| | f) e) + annealed 75 hours at 250°C, quenched | h ₁ 00 line r.t. data only |
| | g) Annealed 5 hours at 850°C, quenched, and annealed (uninterrupted) 168 hours at 250°C, quenched | h ₁ h ₂ 0 plane r.t. data and 136°K data |
| | h) Annealed 6 hours at 800°C, furnace cooled to 375°C, annealed 80 hours at 375°C, quenched | h ₁ h ₂ 0 plane r.t. data only |

* r.t. = room temperature

All annealing was done in H₂ and the quenching medium was room temperature water.

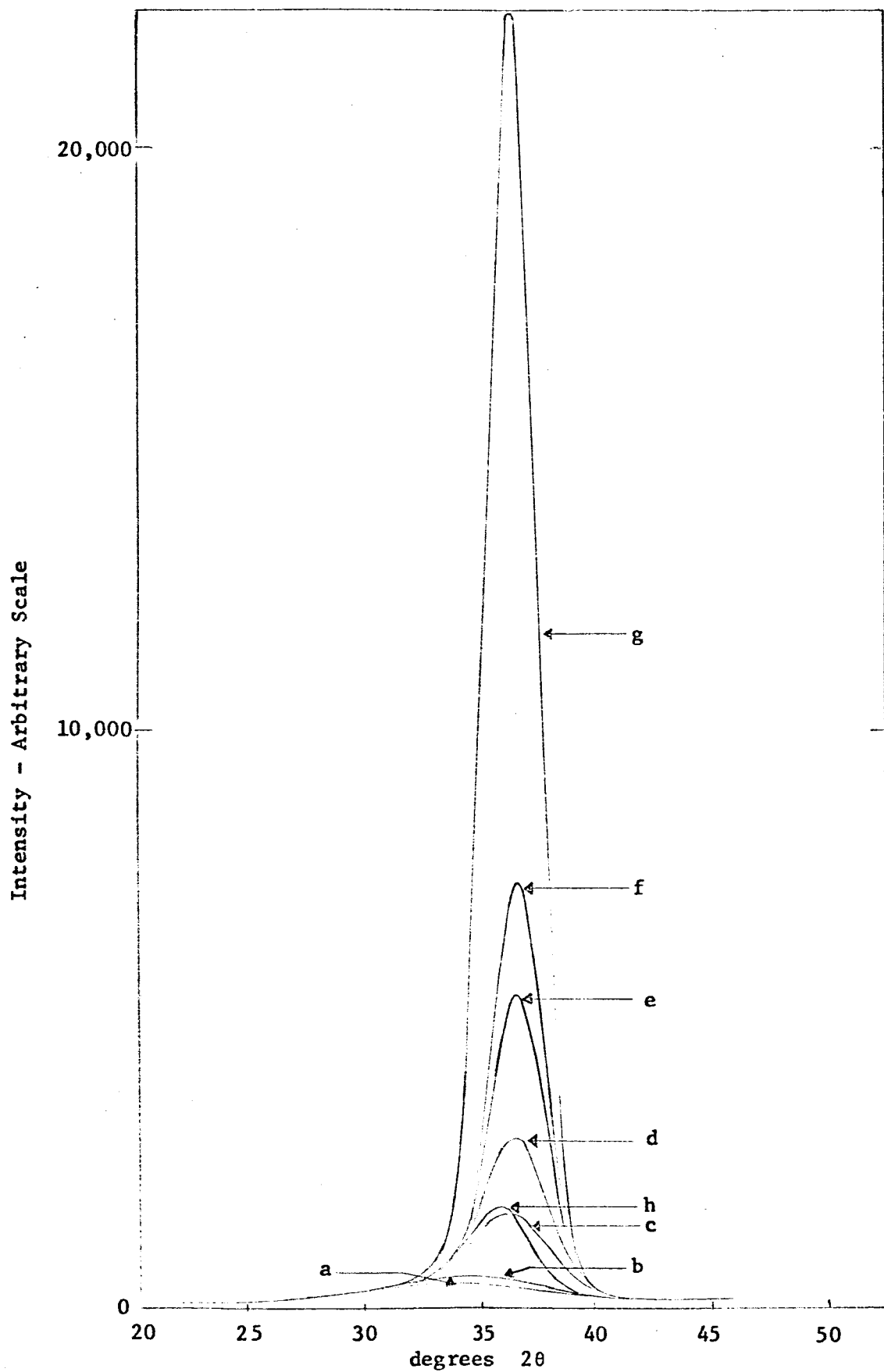


Figure 2. Intensity distribution along the h_{100} line in reciprocal space near 100 for an Fe-19.2 at. % Al sample given various heat treatments. The letters a through g refer to the treatments indicated in Table I.

long range order exists. The two-dimensional data showed that the long range ordered state attained after holding 168 hours at 250°C corresponded to the Fe Al type rather than the Fe_3Al type. This observation apparently means that the Fe_3Al ordered region in the Fe-Al equilibrium diagram is completely surrounded by the Fe Al ordered region.

A problem was encountered when we tried to interpret the data taken throughout a plane in reciprocal space quantitatively and obtain two-dimensional short range order parameters. In this interpretation it is necessary to know the atomic scattering factors of Fe and Al quite accurately. Furthermore, when Co K α radiation is used for the study of Fe bearing samples a significant Hönl dispersion correction to the usual atomic scattering factors must be applied due to the proximity of the Co K α wavelength to the K absorption edge of Fe. To our surprise we found that reliable values of this correction for the case of Fe bearing samples and Co K α radiation were not available in the literature. Because of the need for accurate values of the atomic scattering factors of Fe and Al in the interpretation of our diffuse scattering measurements, and, also, because the measurements should be useful to other investigators who wish to use Co K α radiation for x-ray studies on Fe-bearing samples, we decided that the best course would be to determine the values of the atomic scattering factors of Fe and Al to be used with Co K α radiation experimentally.

In order to assess experimentally the appropriate value of the atomic scattering factor of Fe and Al to be used when Co K α radiation is used, several powder compacts of carbonyl iron (>99.9% purity) and high purity Al were prepared. The starting powders were each -325 mesh. Exper-

iments were performed to determine the appropriate compacting pressure so as to obtain a compact which was free of preferred orientation. The compacts which were finally used were pressed with the following pressures:

Fe: 20 ksi, 25 ksi, 27.5 ksi, 30 ksi

Al: 4 ksi, 5 ksi, 5.5 ksi, 6.0 ksi, 6.5 ksi, 7 ksi

The intensity profile of each Bragg reflection which could be reached using our diffractometer and Co K α radiation was measured for each of the compacts listed above. The procedure used for these measurements was point counting for 50 seconds at positions separated by $1/4^\circ$ 2θ through each Bragg reflection and well into the background intensity on either side. Since the experimental arrangement was the same as that used for the single crystal diffuse scattering measurements, the $1/4^\circ$ increments in 2θ proved sufficiently small to accurately define the shape of each reflection. Integrated intensities in arbitrary units were computed by determining the area above background under each profile using Simpson's rule. By this means the integrated intensities of the 110, 200, 211, and 220 reflections from Fe and the 111, 200, 220, 311, 222, and 400 reflections of Al were determined. No systematic differences were observed between the results obtained from compacts prepared with different pressing conditions in the range given above. The results from the various compacts were, therefore, averaged. Also a correction for the temperature diffuse scattering included in the measured integrated intensities was applied according to the method described by Chipman and Paskin (2).

The integrated intensity, $\int I d(2\theta)$, of a reflection from a powder is given by

$$\int I d(2\theta) = \frac{P_o}{8\pi R^2} \frac{e^4}{m^2 c^4} \frac{1 + \cos^2 2\theta_m \cos^2 2\theta}{1 + \cos^2 2\theta_m} \frac{j \lambda^3 F_{hkl}^2 e^{-2m}}{2 \mu V_c^2 \sin 2\theta \sin \theta} \quad (1)$$

where

- P_o = power in the incident beam
 R = specimen to counter distance
 e = charge of an electron
 m = mass of an electron
 c = velocity of light
 θ_m = Bragg angle for the monochromator crystal
 θ = Bragg angle for the hkl reflection from the sample
 λ = wavelength of radiation
 j = multiplicity factor for (hkl) planes
 μ = linear absorption coefficient for the sample
 V_c = volume of the unit cell of the sample
 F = structure factor of sample
 e^{-2m} = temperature factor

The intensity scattered from an amorphous standard such as polystyrene at a fixed angle θ' is given by

$$I' = \frac{P_o N}{2 \text{ mol.wt.} (\mu'/\rho')} \frac{e^4}{m^2 c^4 R^2} \frac{1 + \cos^2 2\theta_m \cos^2 2\theta'}{1 + \cos^2 2\theta_m} \left(\frac{I_{eu}}{M} \right)' \quad (2)$$

where

- N = Avogadro's number
 $\left(\frac{I_{eu}}{M} \right)'$ = the intensity scattered from polystyrene in "electron units" per molecule at θ' .

Taking the ratio of equation 1 to equation 2 and solving for $F^2 e^{-2m}$:

$$F^2 e^{-2m} = \frac{8\pi N \mu V_c^2 \sin 2\theta \sin \theta}{\text{mol.wt.} (\mu'/\rho') j \lambda^3} \left(\frac{I_{eu}}{M} \right)' \cdot \frac{f I_d(2\theta)}{I'} \frac{1 + \cos^2 2\theta_m \cos^2 2\theta'}{1 + \cos^2 2\theta_m \cos^2 2\theta} \quad (3)$$

Using equation 3 and measured values of $\int I_d(2\theta)$, and I' , $F^2 e^{-2M}$ can be calculated if $(I_{eu}/M)'$ is known. In the present research I' was the measured scattering from polystyrene at $126^\circ 2\theta$ for which $(I_{eu}/M)'$ is 63.2. Since Fe is bcc and Al is fcc, we have

$$F_{Fe}^2 e_{Fe}^{-2M} = 4 f_{Fe}^2 e_{Fe}^{-2M}$$

and

$$F_{Al}^2 e_{Al}^{-2M} = 16 f_{Al}^2 e_{Al}^{-2M},$$

where the f 's are the atomic scattering factors. The experimentally determined values of $f_{Fe}^2 e_{Fe}^{-2M}$ and $f_{Al}^2 e_{Al}^{-2M}$ are presented in Table II.

The temperature factor, e^{-2M} can be evaluated from previously determined values of the Debye temperature. Batterman, Chipman, and De Marco (3) give a Debye temperature of $425^\circ K$ for Fe and a value of $395^\circ K$ for Al. With these values for the Debye temperature, values of $|f|$ for Co K α radiation are as presented in Table II. These values may be compared to the calculated atomic scattering factors, f_o , as obtained from the International Tables for X-Ray Crystallography, Vol. III, pp. 202-205. The difference $|f| - f_o$ is an estimate of the Hönl dispersion correction to be applied to f_o when Co K α radiation is used.

At the present time we are proceeding with the interpretation of the diffuse scattering measurements using the experimentally determined values of $|f|$. In the near future we expect to prepare a more complete report and discussion of the measured values of $|f|$ as well as of our diffuse scattering measurements on Fe-Al alloys.

TABLE II
EXPERIMENTALLY DETERMINED VALUES OF THE ATOMIC
SCATTERING FACTORS OF IRON AND ALUMINUM FOR Co K α RADIATION

Sample: Fe

| hkl | 2 θ | $f^2 e^{-2M}$ | $ f *$ | f_o | $ f - f_o$ |
|-----|------------|---------------|--------|-------|-------------|
| 110 | 52.85 | 177.93 | 13.58 | 18.37 | -4.79 |
| 200 | 77.68 | 102.71 | 10.59 | 15.19 | -4.60 |
| 211 | 100.20 | 66.06 | 8.68 | 13.06 | -4.38 |
| 220 | 124.50 | 45.22 | 7.34 | 11.56 | -4.22 |

Sample: Al

| hkl | 2 θ | $f^2 e^{-2M}$ | $ f *$ | f_o | $ f - f_o$ |
|-----|------------|---------------|--------|-------|-------------|
| 111 | 45.40 | 69.17 | 8.65 | 8.91 | -0.26 |
| 200 | 52.80 | 59.82 | 8.15 | 8.49 | -0.34 |
| 220 | 77.84 | 39.97 | 7.02 | 7.31 | -0.29 |
| 311 | 94.62 | 30.00 | 6.33 | 6.63 | -0.30 |
| 222 | 100.36 | 27.23 | 6.02 | 6.43 | -0.41 |
| 400 | 124.60 | 19.36 | 5.42 | 5.76 | -0.34 |

* Assuming $\theta_{Fe} = 425^\circ K$ and $\theta_{Al} = 395^\circ K$

IV. THE NICKEL-TUNGSTEN SYSTEM

In order to study the relationship of the local atomic arrangements in Ni-rich Ni-W solid solutions to their physical and thermal properties, the following set of specific goals were chosen:

1. Growth of a large single crystal of Ni -10 at. % W and the investigation of the local atomic arrangements in this alloy after various heat treatments by the single crystal x-ray diffuse scattering technique.
2. Measurement of the specific heat as a function of temperature for a previously annealed sample of Ni -10 at. % W alloy.
3. Measurement of resistivity changes as a function of per cent reduction in area by swaging and after various recovery heat treatments in Ni -5 and 10 at. % W alloys.
4. Correlation of the resistivity measurements with diffuse scattering measurements made on cold worked and on recovered polycrystalline samples of Ni -5 and 10 at. % W alloys.
5. Measurement of the stored energy of deformation in Ni -5 and 10 at. % W alloys.

Most of the experimental work outlined above was completed during the present report period. The interpretation of these experimental results is presently being carried out in conjunction with the preparation of a final report covering our research relative to the Ni-W system. Since this final report should soon be available, these results will not be presented or discussed further in this status report.

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